

CLAIMS

What is claimed is:

1. A process for preparing a mixture comprising levulinic acid esters and  
5 formic acid esters from biomass, the process comprising the steps of:
  - (a) contacting the biomass with water in the presence of a first acid catalyst to form a first reaction mixture comprising levulinic acid, formic acid and furfural, the first reaction mixture having a liquid phase and, optionally, a solid phase;
  - 10 (b) optionally, separating the liquid phase from the solid phase of the first reaction mixture to form a second reaction mixture;
  - (c) removing the furfural from the first reaction mixture or the second reaction mixture to form a third reaction mixture;
  - (d) contacting the first reaction mixture, the second reaction  
15 mixture, or the third reaction mixture with at least one olefin, optionally, in the presence of a second acid catalyst, to produce a fourth reaction mixture, the fourth reaction mixture having an organic phase and an aqueous phase;
  - (e) separating the organic phase containing levulinic acid esters  
20 and formic acid esters from the aqueous phase of the fourth reaction mixture; and
  - (f) optionally, isolating the mixture comprising levulinic acid esters and formic acid esters from the organic phase of step (e).
- 25 2. A composition comprising levulinic acid esters and formic acid esters, made by a process comprising the steps of:
  - (a) contacting the biomass with water in the presence of a first acid catalyst to form a first reaction mixture comprising levulinic acid, formic acid and furfural, the first reaction mixture having a liquid  
30 phase and, optionally, a solid phase;
  - (b) optionally, separating the liquid phase from the solid phase of the first reaction mixture to form a second reaction mixture;

- (c) removing the furfural from the first reaction mixture or the second reaction mixture to form a third reaction mixture;
- (d) contacting the first reaction mixture, the second reaction mixture, or the third reaction mixture with at least one olefin, optionally, in the presence of a second acid catalyst, to produce a fourth reaction mixture, the fourth reaction mixture having an organic phase and an aqueous phase;
- (e) separating the organic phase containing levulinic acid esters and formic acid esters from the aqueous phase of the fourth reaction mixture; and
- (f) optionally, isolating the mixture comprising levulinic acid esters and formic acid esters from the organic phase of step (e).

3. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst or the second acid catalyst, independently, is a soluble acid catalyst with a pKa less than 4, or a metal salt thereof.

4. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst or the second acid catalyst, independently, is a soluble acid catalyst with a pKa less than 2, or a metal salt thereof.

5. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst or the second acid catalyst, independently, is a heterogeneous acid catalyst having an  $H_0$  of less than or equal to 2.

6. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst and the second acid catalyst, independently, are selected from the group consisting of inorganic acids, organic sulfonic acids, heteropolyacids, perfluoroalkyl sulfonic acids, metal salts thereof, mixtures of metal salts, and combinations thereof.

7. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst and the second acid catalyst, independently, are selected

from the group consisting of zeolites; CBV-3020 zeolite; fluorinated alumina; acid-treated silica; acid-treated silica-alumina; acid-treated titania; acid-treated zirconia; heteropolyacids supported on zirconia, titania, alumina, silica; and combinations thereof.

5

8. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst and the second acid catalyst, independently, are selected from the group consisting of metal sulfonates, metal sulfates, metal trifluoroacetates, metal triflates, and mixtures thereof; mixtures of salts  
10 with their conjugate acids,  $\text{Zn}(\text{BF}_4)_2$ , and combinations thereof.

9. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst and the second acid catalyst, independently, are selected from the group consisting of sulfuric acid, fluorosulfonic acid, phosphoric  
15 acid, p-toluenesulfonic acid, benzenesulfonic acid, phosphotungstic acid, phosphomolybdic acid, trifluoromethanesulfonic acid, 1,1,2,2-tetrafluoroethanesulfonic acid, 1,1,1,2,3,4-hexafluoropropanesulfonic acid, bismuth triflate, yttrium triflate, ytterbium triflate, neodymium triflate, lanthanum triflate, scandium triflate, zirconium triflate, and combinations  
20 thereof.

10. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst and the second acid catalyst, independently, are used in an amount of from 0.01% to 5% by weight of the reactants.

25

11. The process of claim 1 or the composition of claim 2, wherein the first acid catalyst and the second acid catalyst, independently, are used in an amount of from 0.25% to 2.5% by weight of the reactants.

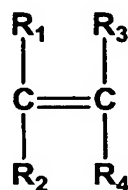
30 12. The process of claim 1 or the composition of claim 2, wherein in step (b), the solid phase is separated from the liquid phase by a liquid-solid separation method selected from a group consisting of sedimentation,

filtration, centrifugation, decantation, thickening, spray drying, evaporation, and combinations thereof.

13. The process of claim 1 or the composition of claim 2, wherein in step  
5 (c), the furfural is separated by a liquid-liquid separation method.

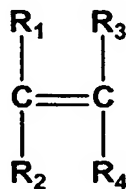
14. The process of claim 1 or the composition of claim 2, wherein the  
olefin is selected from the group consisting of compounds having formula  
(I), wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently hydrogen or an alkyl  
10 group, and optionally, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> form a ring independently with  
each other to form a cyclic or bicyclic alkyl group, and wherein the total  
number of carbons in the compound is not more than twenty two.

(I)



15. The process of claim 1 or the composition of claim 2, wherein the  
olefin is selected from the group consisting of compounds having formula  
(I), wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently hydrogen or an alkyl  
group, and optionally, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> form a ring independently with  
each other to form a cyclic or bicyclic alkyl group, and wherein the total  
20 number of carbons in the compound is less than nine.

(I)



16. The process of claim 1 or the composition of claim 2, wherein in step (d), said olefin is contacted with said liquid phase in the presense of at least one water-immiscible solvent.

5 17. The process of claim 1 or the composition of claim 2, wherein in step (d), the organic phase and the aqueous phase are separated by a process selected from a group consisting of reactive extraction, liquid-liquid extraction, distillation, absorption, membrane separation, decantation, and combinations thereof.

10

18. The composition of claim 2 used as a fuel, an oxygenate for gasoline, an octane number-enhancing agent for gasoline, an oxygenate for diesel, a cetane number-enhancing agent for diesel or a fuel additive for biofuel.

15 19. A gasoline, diesel or biofuel comprising from 1% to 90% by volume of the composition of claim 2.

20. A gasoline, diesel or biofuel comprising from 1% to 50% by volume of the composition of claim 2.

20

21. A gasoline, diesel or biofuel comprising from 1% to 20% by volume of the composition of claim 2.

22. A process for manufacturing a fuel additive, the process comprising  
25 the process of claim 1.

23. A process for manufacturing a gasoline, a diesel fuel or a biofuel, the process comprising the process of claim 1.